standard we know, the first the elimination of the recognized sources of error, second the repetition of the observations so that the constancy of the phenomenon is assured. We can not do more than allude to this theme, which I must leave to the future and to a more competent mind to analyze and develop.

To sum up: The method of science is not special or peculiar to it, but only a perfected application of our human resources of observation and reflection—to use the words of von Baer, the greatest embryologist. To secure reliability the method of science is *first,* to record everything with which it deals, the phenomena themselves and the inferences of the individual investigators, and to record both truly; *second,* to verify and correlate the personal knowledges until they acquire impersonal validity, which means in other words that the conclusions approximate so closely to the absolute truth that we can be safely and profitably guided by them. The method of science is no mystic process. On the contrary, it is as easily comprehended as it is infinitely difficult to use perfectly and at its best the method supplies merely available approximations to the absolute.

We set science upon the throne of imagination, but we have crowned her with modesty, for she is at once the reality of human power and the personification of human fallibility.

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## *THE FORMATION OF CARBOHYDRATES IN THE VEGETABLE KINGDOM*[1]

THE classical discovery of Woehler in 1828 first revealed to chemists the possibility of the synthetic production of those compounds which occur naturally in the members of the animal and vegetable kingdoms. Woehler himself evidently realized the importance of his discovery. Thus, in a letter to his old teacher, Berzelius, he wrote:[2]

> You may remember how, while I was with you, when trying to make ammonia combine with cyanic acid, I always obtained a crystalline body which gave the reactions of neither the one body nor the other. I have just made this crystalline body the subject of a little investigation, preparing it by the action of ammonia on lead cyanate and have discovered it to be nothing less than urea.

Then he significantly adds, "This may be taken as an artificial production from inorganic substance."

The idea, however, that such compounds could be formed only through the agency of the vital forces of the living organism was one of such long standing and was so deeply established in the popular belief that even the chemists contemporaneous with Woehler were slow to grasp the full significance of the discovery. Berzelius himself was evidently not convinced, since in his text-book published in 1837, nine years after Woehler's discovery, he expressed doubt as to the possibility of being able to discover the differences between the causes of reactions in the living organism and those in the inorganic realm. Likewise Gerhardt[3] wrote seven years later (1842) as follows: "I have shown that the chemist works in a way altogether opposite from living nature. The one burns, destroys, operates by analysis. Vital force alone operates by synthesis and reconstructs the edifice torn down by chemical forces."

Other discoveries, however, of a nature

[1] Address of the vice-president and chairman of Section C—Chemistry—at the Minneapolis meeting of the American Association for the Advancement of Science.

[2] "Berzelius-Woehler Briefwechsel," I., p. 206; Armitage, "A History of Chemistry," p. 143.

[3] *Compt. rend.*, 15, p. 498. Bunge, "Text-book of Organic Chemistry," p. 1.

similar to Woehler's followed, although somewhat tardily. Kolbe in 1845 showed that it was possible to synthesize acetic acid from its elements. Berthelot in 1854 likewise built up the fats. In the light of such achievements the most skeptical could no longer maintain the old view concerning the impossibility of building up in the laboratory from inorganic sources those compounds naturally occurring in the living organism. The recognition of this great truth opened up to chemists a new line of investigation and from that time the synthetic preparation of organic compounds has ever been a fruitful field of research. It has sometimes seemed to me, however, that in the enthusiasm over the discoveries which chemists have made in this field of investigation we are inclined to over-estimate the work done, great as that may be, and perhaps unintentionally convey the impression that the chemical changes taking place in the living organism are thoroughly understood and can be duplicated in the laboratory. While of course it is true that many of the compounds in the living organism have been synthesized and that the number of such syntheses is constantly increasing, yet we must not forget that the chemist's method has never been, in detail at least, the method of nature. Indeed, as a rule they are widely divergent. We are apt to employ powerful reagents many of which so far as is known do not exist in the organism nor in the mediums from which it draws its sustenance. The drastic treatment to which these substances are often subjected and the temperatures at which the reactions are carried on are all in the greatest contrast to the conditions which prevail in the organism in which the natural synthesis is effected. In a few cases the laboratory methods employed more nearly approach the conditions which prevail in nature and such syntheses always have a greatly added interest at least from a theoretical standpoint. Thus the observation of Loew[4] that a sugar-like compound could be formed by the condensation of formaldehyde was exceedingly important, but this importance was greatly enhanced by the fact that this condensation could be effected by the action of mild alkalis or even neutral substances at ordinary temperatures—conditions which approximate those existing in the growing plant. Likewise the importance of the observations of Lobry de Bruyn and van Ekenstein[5] that the three hexoses, namely, mannose, fructose and dextrose, are mutually convertible, lay largely in the fact that these transformations could be made to take place at ordinary temperatures under the influence of reagents that may exist in the soil. The study of such problems as these has become not only one of the most alluring and fascinating in the fields of research in organic chemistry, but their solution is fraught with the greatest significance, since it will be a step in the direction of gaining some understanding of the mysteries of life itself.

Inasmuch as the carbohydrates play such an important part in the economy of the vegetable kingdom, it is quite natural that the investigations of the problems pertaining to the synthesis of compounds in the living organisms have been largely directed towards this class of compounds. Since it is impossible in a short time to discuss with any thoroughness the various researches carried out in this field of investigation I will confine myself to those which have some important bearing upon the well-known hypothesis proposed by Baeyer, with a view of determining, if pos-

[4] *J. prakt. Chem.*, 33, p. 321.

[5] *Ber. d. chem. Gesell.*, 28, p. 3078.

sible, its standing in the light of modern discoveries.

In 1861 there appeared in the *Annalen der Chemie* and simultaneously in the *Comptes rendus* a short article by a Russian chemist, Butlerow,[6] in which he described the formation of a sugar-like substance (methylenitan, he termed it) through the interaction of trioxymethylene and calcium hydroxide in an aqueous solution. Although the resulting substance was optically inactive and was not fermentable, Butlerow nevertheless was sure that the sweet syrup which he obtained contained a sugar, for he concludes his accounts with the statement that his results furnish the first example of the synthesis of a sugar-like body. These results of Butlerow proved to be of the greatest importance, not only because of the facts revealed, but also because they served to suggest to other investigators the method of attacking the general problem of the synthetic production of sugars. Moreover, they undoubtedly served as an experimental groundwork upon which Baeyer a few years later based his well-known hypothesis.

The essential assumptions of Baeyer's hypothesis, viz., the production of formaldehyde through the interaction of carbon dioxide and water, and the subsequent polymerization of this to a sugar, are well known to all and require no discussion. It may be of interest, however, to recall some of the reasons advanced by Baeyer in setting forth these assumptions.

The original statement of the theory was published in the *Berichte* just forty years ago (1870) and was entitled "Ueber die Wasserentziehung und ihre Bedeutung für das Pflanzenleben un die Gährung."[7]

[6] *Annalen der Chem.*, 120, p. 295; *Compt. rend.*, 53, p. 145.

[7] *Ber. d. chem. Gesell.*, 3, p. 67,

Baeyer here calls attention to the fact that in the transformation of the compounds of carbon, hydrogen and oxygen, the separation of water plays just as weighty a rôle as do the processes of oxidation and reduction. He then discusses the groups of those reactions in which water is formed by the union of hydrogen and oxygen withdrawn from the interacting compounds. Among the various reactions are those in which the water removed is formed by the union of hydrogen taken from one molecule with an hydroxyl group taken from a different molecule—an "*äussere Condensation,*" as Baeyer termed it. To illustrate this he gives his interpretation of the reaction involved in Butlerow's sugar synthesis. Although Butlerow had used trioxymethylene, Baeyer evidently felt justified, because of the intimate relation between this compound and formaldehyde, in assuming that the reaction actually taking place is one between the different molecules of formaldehyde. Considering that formaldehyde in aqueous solution is in the hydrated form, Baeyer shows that by the splitting off of water formed by the union of a hydroxyl group from one molecule of formaldehyde with the hydrogen from another molecule and the union of the two remaining residues through the resulting free affinities, it is easy to understand how from six molecules of formaldehyde the hexoses might result. Baeyer even deduced two possible structural formulas for a hexose based on this interpretation of the course of the reaction, one of these being the well-known aldehyde formula. Likewise he shows how by the condensation of three molecules of formaldehyde one would expect to obtain an aldehyde of glyceric acid. The older view of Liebig to the effect that the fruit acids are the intermediate products from which the sugars result, Baeyer rejects in favor of

the one that the sugars are formed directly from the carbonic acid. This formation could be satisfactorily accounted for as follows: Through the combined action of chlorophyll and sunlight carbon dioxide suffers dissociation into carbon monoxide and oxygen. The oxygen is evolved while the carbon monoxide combines with the chlorophyll much as it does with the hæmoglobin of the blood. By the action of hydrogen, obtained by the dissociation of water, the carbon monoxide is then changed into formaldehyde from which the sugar results by condensation. The essential points in Baeyer's hypothesis are therefore, first, the production of formaldehyde from carbon dioxide and water, and second, the formation of sugars by the polymerization of the aldehyde. Other investigators have suggested certain modifications of this theory, mainly in the method of generation of the formaldehyde. Thus, Erlenmeyer[8] in 1877 from certain observations made on the action of water on hydroxy acids was led to conclude that the carbonic acid would be acted upon by water under the conditions existing in the plant with the production of formic acid and hydrogen peroxide in accordance with the following equation: $HO.COOH + HOH \rightarrow H_2O_2 + H.COOH$. The formaldehyde would then result from the reduction of the formic acid. Bach,[9] on the other hand, assumes the decomposition of the carbonic acid directly into formaldehyde and an unstable percarbonic acid, $H_2CO_4$, which would break down into hydrogen peroxide with regeneration of carbon dioxide. Usher and Priestley[10] as well as Pollacci[11] have also suggested certain modifications of the general assumptions.

[8] *Ber. d. chem. Gesell.*, 10, p. 634.

[9] *Compt. rend.*, 116, pp. 1145, 1389; 126, p. 479.

[10] *Proc. Royal Soc.*, B, 77, p. 369; 78, p. 318.

[11] *Bot. Zentralbl.* for 1904 and 1905.

The principal researches which have a direct bearing on the validity of Baeyer's hypothesis may be classified in regard to their bearing on the following problems: First, Is it possible to produce formaldehyde in the laboratory from carbon dioxide and water under conditions approximating those existing in the plant? Second, Is formaldehyde actually present in the living organism? Third, Is it possible for the organism to assimilate formaldehyde? Fourth, Is it possible to produce carbohydrates directly from formaldehyde?

It is my purpose to discuss briefly the more important researches carried out in these fields of investigation.

### PRODUCTION OF FORMALDEHYDE THROUGH THE REDUCTION OF CARBONIC ACID

The production of formaldehyde through the reduction of water and carbon dioxide has been the subject of numerous researches. Maly[12] in 1865, and in more recent time Lieben[13] (1895), attempted this reduction by employing various amalgams as reducing agents. Royer[14] in 1870 and Coehn and Jahn[15] in 1904, on the other hand, studied the effect of electrolytic hydrogen on the carbonic acid. In all these cases, however, the reduction resulted not in the formation of formaldehyde, but of formic acid. In 1893 Bach[16] attempted to carry out the reaction under conditions closely approximating those existing in the plant. As a substitute for the chlorophyll in the plant Bach, relying upon the well-known sensitiveness of uranium compounds to light, used uranium acetate as a chemical and photo-sensitizer. Carbon dioxide was passed through flasks filled

[12] *Annalen der Chem.*, 135, p. 119.

[13] *Wien. Monats.*, 16, p. 211; 18, p. 582.

[14] *Compt. rend.*, 70, p. 731.

[15] *Ber. d. chem. Gesell.*, 37, p. 2836.

[16] *Compt. rend.*, 116, pp. 1145, 1389.

with a 1.5 per cent. solution of uranium acetate. When the experiment was carried out in the sunlight there was obtained a precipitate of the hydroxides of uranium together with a small amount of peroxide. The results are explained on the supposition that the carbonic acid is resolved into formaldehyde and a percarbonic acid, $H_2CO_4$, in accordance with the following equation: $3H_2CO_3 = CH_2O + 2H_2CO_4$. The percarbonic acid as fast as formed breaks down into hydrogen peroxide and carbon dioxide. To support this interpretation of the course of the reaction, Bach refers to the work of Wurster,[17] who claimed to have demonstrated the presence of hydrogen peroxide in plants, although Wurster's results had been strongly challenged by Bokorny.[18] In 1898 Bach[19] again returned to the problem, this time using palladium as a catalyzer. Carbon dioxide was passed through water containing palladium held in suspension. In the clear liquid obtained by filtering off the palladium Bach claims to have established the presence of formaldehyde.

While the experiments of Bach are ingeniously conceived and are of great interest, his interpretation of the results do not appeal to one as at all conclusive. The most that can be said is that the generation of formaldehyde and hydrogen peroxide under the conditions of the experiments is probable. Their presence must be regarded as inferred rather than proved. It is not strange therefore that his results have been criticized. In 1904 Euler[20] repeated the work and concluded that the carbon dioxide in Bach's experiments did not enter into the reaction at all since exactly the same results are obtained if one substitutes a current of hydrogen or nitrogen for the carbon dioxide.

On the other hand, Usher and Priestley[21] in 1906 reported that "the experiments of Bach have been repeated and confirmed, both as to the production of peroxide and formaldehyde." Oddly enough, however, they gave no account as to their manner of confirming these results, and since Bach himself rather inferred than proved the presence of these two compounds the statement of Usher and Priestley is not wholly satisfactory. In order to meet the criticism that the production of formaldehyde in Bach's experiments may have resulted from the reduction of the acetic acid which would undoubtedly be formed by the hydrolysis of the uranium acetate used, Usher and Priestley[22] in a later article described a series of experiments in which uranium sulphate was substituted for the uranium acetate. In these experiments no formaldehyde could be detected, although the authors report that "a study of the reactions involved favors the view that it is formed as a transitory intermediate product." In their original work Usher and Priestley were led to conclude from experiments on plants (*Elodea* were used) that the generation of formaldehyde in the plant from carbon dioxide and water is not a vital process at all since small plants of *Elodea* in which all life had been destroyed by immersion in boiling water accumulated perceptible amounts of formaldehyde when exposed to sunlight in a moist atmosphere of carbon dioxide. The tests for formaldehyde were made directly upon the leaves as well as upon the distillate from the leaves. The principal tests employed were (*a*) the development of color in Schiff's reagent, (*b*) the formation of methyleneaniline with

[17] *Ber. d. chem. Gesell.*, 19, p. 3195.

[18] *Ber. d. chem. Gesell.*, 21, p. 1100.

[19] *Compt. rend.*, 126, p. 479.

[20] *Ber. d. chem. Gesell.*, 37, p. 3411.

[21] *Proc. Royal Soc.*, B, 77, p. 370.

[22] *Proc. Royal Soc.*, B, 78, p. 318.

aniline, and (c) the formation of hexamethylene tetramine with ammonia and bromine. Acting on the conclusion that the production of formaldehyde in the plant is not a vital process, these investigators in a later article described a series of experiments in which they attempted to produce formaldehyde from water and carbon dioxide in the laboratory by reproducing the conditions existing in the plant. Plates of glass were painted over with gelatine, which in turn was coated with a thin film of chlorophyll. The plates so prepared were placed in a moist atmosphere of carbon dioxide and exposed to the sunlight. The chlorophyll was employed to effect a reduction of the carbon dioxide and water into formaldehyde by acting as a photo-sensitizer, while the gelatine was used in the hope that it would absorb all formaldehyde as fast as formed, thus removing it from the sphere of action. After the exposure of the plate the gelatine was removed and tested for formaldehyde by the tests previously mentioned and in all cases the aldehyde was found to be present.

If the interpretation of these results, as given by Usher and Priestley, is correct, this work is of the very highest value, not only in its relation to Baeyer's hypothesis, but especially because the reduction of carbon dioxide and water to formaldehyde in plants is shown to be a laboratory and not a vital process. It must be stated, however, that the conclusions reached have been contradicted by Ewart,[23] who insists that the gelatine used in the experiments will give the test for formaldehyde just as well before exposure to carbon dioxide and light as after such exposure; and that even granting the generation of formaldehyde under these conditions, it is, to say the least, just as reasonable to conclude that it is derived from the decomposition of the chlorophyll in the presence of oxygen as it is to conclude that it is formed from carbon dioxide and water.

Some of the most interesting results in this field of investigation have been obtained by Löb,[24] who attempted to gain some insight into the changes taking place in the plant by substituting the action of the silent electric discharge for that of the sunlight as well as of any catalytic agent or enzyme present in the plant. In this way it was shown that formaldehyde is a direct reduction product of carbon dioxide and water vapor. Löb claims, and with justice, that his experiments bring the first positive proof that formaldehyde is a direct reaction product of moist carbon dioxide.

In 1907 Fenton[25] attempted the generation of formaldehyde directly from carbonic acid by passing a current of carbon dioxide for a number of hours through pure water in contact with several rods of amalgamated magnesium. He concludes that "the solution gives slight but unmistakable indications of formaldehyde" with certain standard color tests. So far as I know, these results have not been challenged.

The most recent work, as well as probably the most significant, is that of Berthelot and Gaudechon.[26] By the action of ultra-violet light on a mixture of carbon dioxide and water vapor, these investigators have succeeded in obtaining formaldehyde together with carbon monoxide and oxygen. Under the same conditions, carbon monoxide and water vapor gives rise to formaldehyde, carbon dioxide and hydrogen.

[23] *Proc. Royal Soc.*, B, 80, p. 30.

[24] *Zeit. f. Elektrochem.*, 12, p. 282.

[25] *J. L. Chem. Soc.*, 91, p. 687.

[26] *Compt. rend.*, 150, p. 1690.

## THE EXISTENCE OF FORMALDEHYDE IN PLANTS

As an immediate result of Baeyer's hypothesis attempts have been made to detect formaldehyde in plants of various species and grown under various conditions. The results of these investigations are not at all satisfactory and indeed consist largely in affirmations and denials. The problem, however, is not a simple one. In the first place formaldehyde, if present at all, can only be present in very minute quantities because of its very great toxicity, and while it is true that extremely delicate tests have been advanced for formaldehyde it is likewise true that these tests have been subjected to considerable criticism. Moreover, it is possible that such delicate tests might be influenced by the presence of various other substances present in the plant.

In 1881 Loew and Bokorny[27] advanced the theory that the vital force of the living protoplasm is essentially connected with the presence of aldehyde groups in the substance forming the protoplasm. When certain algæ, for example, were immersed in a dilute solution of silver nitrate the living cells were found to be darkened when examined under the microscope. The authors attribute this change in color to the reduction of the silver salt by the aldehyde present. Plants previously immersed in boiling water to destroy the life of the protoplasm failed to give the test; hence the authors conclude that the aldehyde group disappears with the life of the plant.

In the same year Reinke[28] by macerating certain green leaves (those of the grape vine, the poplar, the willow and conifers, were tested) and distilling the mass in a current of steam obtained a liquid having strong reducing powers which he attributed to the presence of an aldehyde. Moreover, the aldehyde must be an easily volatile one, for it is present chiefly in the first portions of the distillate. While not able to prove the exact identity of the aldehyde Reinke concluded that it is formaldehyde. These reactions were obtained only in the case of chlorophyll-bearing plants. Reinke suggested that the reducing power of the algæ observed by Loew and Bokorny might be due to the presence of formaldehyde in the plant. This statement led to further studies by both investigators and the publication of several articles[29] in which each held to his original interpretation of the results, although Reinke was forced to admit that he had not definitely proved the presence of formaldehyde in the distillate from the plants, but only the presence of an easily volatile aldehyde.

Mori[30] (1882) experimenting with the leaves of the rose bush and of oats obtained results similar to those of Reinke. He also tested the plant by adding a few drops of Schiff's reagent directly to portions of the plant, whereupon a red color gradually resulted. Loew and Bokorny[31] claim, however, that the development of the color in Mori's experiments was due to the evaporation of the sulphurous acid in Schiff's reagent and show that this reagent gradually becomes colored by mere exposure to air.

In 1889 Polacci[32] reported the results of an extended series of investigations from

[27] *Arch. ges. Physiol.* (*Pflügers*), 25, p. 150.

[28] *Ber. d. chem. Gesell.*, 14, p. 2144.

[29] *Bot. Zeit.*, 1882, No. 40; *Ber. d. bot. Gesell.*, 15, p. 201; 17, p. 7; *Ber. d. chem. Gesell.*, 15, pp. 107, 695; "Studien über das Protoplasma," zweite Folge, Berlin, 1883.

[30] *Nuovo. Gio. Bot. Ital.*, 14, p. 147.

[31] *Bot. Zeit.*, 1882, p. 832; *Arch. ges. Physiol.* (*Pflügers*), 26, p. 50.

[32] *Atti d. Inst. Bot. d. Univ. d. Pavia*, II., Serie 7, 1.

which he concluded that formaldehyde is undoubtedly present in the green parts of living plants when exposed to sunlight. He experimented directly with the growing plant, as well as with the liquid obtained by distilling the leaves in a current of steam. Twigs were bent down from the growing plant into cylinders containing Schiff's reagent. It was found that when the experiment was carried on in the sunlight the red color gradually developed, which result was attributed by the investigator to the production of formaldehyde. While the results obtained by the tests made directly upon the leaves were only suggestive and not conclusive, the distillate from the leaves Polacci affirms undoubtedly contains formaldehyde itself. Many tests were employed. Some of these were of a general character, while others were definite for formaldehyde itself. Special stress is placed on (*a*) the color test obtained by successive additions of phenylhydrazine, nitroprussiate of sodium and alkali; (*b*) the color test with sulphuric acid and codeine; (*c*) Trillat's color test with an aqueous solution of dimethyl aniline in the presence of acetic acid and lead peroxide; (*d*) the reaction with phenylhydrazine; (*e*) the color test with phenol and sulphuric acid. A short time after the publication of the results of Polacci's experiments two other Italian investigators, namely Plancher and Ravenna,[33] reported a series of similar experiments, but failed to find any conclusive proof of the presence of formaldehyde in plants. The formation of color in Schiff's solution under the conditions of Polacci's experiment was attributed not to the presence of formaldehyde, but to the "active" oxygen evolved by the plant in the process of assimilation. They likewise claimed that the tests which Polacci employed for the detection of formaldehyde in the distillate from green leaves are untrustworthy. In order to determine whether formaldehyde, if present in the green leaves, would actually distill over or would remain combined with compounds in the plants, these investigators added a very dilute solution of formaldehyde to leaves before distillation and then tested for formaldehyde in the distillate. The results showed that the amount of formaldehyde which must be present in the leaves in order to respond to conclusive tests in the distillate is so large that it would destroy at once the vitality of the plants. Polacci's results have also been criticized by Czapeck[34] as being indefinite. Euler,[35] on the other hand, confirms his results, although he expresses the opinion that the formaldehyde is not present in a free state in the plant, but is liberated from its condensation products by the process of distillation. In a more recent article Polacci[36] refers to the criticisms of his investigations and defends his original conclusions with great vigor.

Among the other investigators may be mentioned Grafe[37] as well as Kimpflin,[38] both of whom maintain that formaldehyde is undoubtedly present in the growing plant. The former investigator used a solution of diphenylamine in sulphuric acid as a test, claiming that this reagent gives a green coloration with exceedingly minute quantities of the aldehyde. Kimpflin, on the other hand, recognizing that formaldehyde, if present at all, can only be present in minimal amounts, ingeniously attempts to store up the compound as fast as formed until a sufficient quantity is obtained to respond to the tests. To do

[33] *Atti d. Real. Accad. d. Lincei*, 13, p. 459.

[34] *Bot. Zeit.*, 1900, p. 153.

[35] *Ber. d. chem. Gesell.*, 37, p. 3411.

[36] *Atti d. Real. Accad. d. Lincei*, 16, p. 199.

[37] *Oesterreich. bot. Zeitschrift*, 1906, No. 3.

[38] *Compt. rend.*, 144, p. 148.

this he introduces into the tissue by means of a capillary tube a solution of sodium acid sulphite and methylparamidometacresol. After this injection the plant is exposed to the light for a time, when a section of the leaf is placed in absolute alcohol and subsequently examined under the microscope in the presence of a drop of water. The presence of the aldehyde is shown by the formation of a red color. According to the author, the aldehyde as fast as produced combines with the acid sulphite to form the addition compound which is stable in the absolute alcohol. Upon the addition of a drop of water, however, the aldehyde is liberated and forms a characteristic color with the cresol.

While Usher and Priestley[39] claim to have definitely proved the presence of formaldehyde in the dead plant according to the method described above, they merely infer its presence in the living plant. In fact, they assert that it would be useless to look for it in a healthy living plant because of the rapidity with which it would be transformed into other substances.

In a recent article Bokorny[40] criticizes the work of Kimpflin and others and maintains that the amount of formaldehyde which would have to be present in the plant in order to respond to any of the known tests would certainly destroy the vitality of the plant. He maintains, however, that it is undoubtedly present, but in such minute quantities at any given period that the only hope for its detection lies in the discovery of some agent which would combine with the aldehyde as fast as generated to form a compound that is not toxic to the plant and from which compound it could again be recovered in quantities sufficient to respond to the standard tests. It may be added that this is practically what Kimpflin attempted.

[39] *Proc. Royal Soc.*, B, 77, p. 370.

[40] *Arch. ges. Physiol.* (*Pflügers*), 125, p. 484.

THE ASSIMILATION OF FORMALDEHYDE BY PLANTS

No single evidence perhaps would count so much towards corroborating Baeyer's hypothesis as the proof of the power of plants to assimilate free formaldehyde with the production of carbohydrates. It is natural therefore that many experiments have been made to ascertain just what effect formaldehyde has on the growing plant. In conducting such experiments naturally the formaldehyde would have to be administered in very dilute solutions; moreover, the amount of such solutions would have to be large in order to obtain a sufficient amount of formaldehyde to effect a sensible amount of any assimilation product.

The first investigator to make any extensive study of this question was Bokorny,[41] who attempted to grow certain water plants (green filaments of *Spirogyra*) in dilute solutions of formaldehyde. He found that formaldehyde, even in solutions of 1 to 50,000, was fatal to the growth of the plant. Next the attempt was made to substitute for the free formaldehyde some substance which under the influence of the plant would slowly decompose, giving formaldehyde as one of the decomposition products. Such a substance Bokorny found in methylal which decomposes into formaldehyde and methyl alcohol and also in the sodium acid sulphite addition product of formaldehyde. By the use of these compounds Bokorny hoped to diminish the concentration of the actual aldehyde to the minimum and yet by its constant formation furnish a sufficient amount of it to

[41] *Ber. d. bot. Gesell.*, 1888, p. 119; *Chem. Zeit.*, 44, p. 525; *Phar. Post*, 36, p. 153; *Biolog. Centralbl.*, 12, No. 16 and 17.

the plant to enable one to prove whether or not assimilation actually takes place. It was found that the *Spirogyra* immersed in a solution of either of these substances under certain conditions continue to grow and produce starch in the absence of carbon dioxide. These results must be regarded as strong corroborative evidence in favor of the view that plants have the power of directly assimilating formaldehyde; they are not conclusive, however, since there is no actual proof that the compounds are decomposed by the plants previous to assimilation.

Later Bouillac and Giustiniana[42] succeeded in growing ordinary white mustard in solutions containing traces of formaldehyde. It is interesting to note that a certain amount of light was necessary, however, for the growth of the plant.

Treboux[43] also reports that he has successfully grown the *Elodea* in solutions of one part of formaldehyde in one hundred thousand, but that no starch was formed; hence he concludes that his results are opposed to the general belief that formaldehyde is directly polymerized to carbohydrates.

Usher and Priestley[44] in the investigations referred to above likewise report a case of starch formation in a solution containing one part of formaldehyde in one hundred thousand.

In 1908 Bokorny[45] reported some experiments in which he succeeded in proving that spirogyra can assimilate such substances as glycerol, sucrose and even traces of formaldehyde itself when present in dilute solutions. A year later[46] he again reported some experiments in which he attempted to grow water cress under a bell jar over a 30 per cent. solution of sodium hydroxide containing small amounts of formaldehyde and concludes that the upper portions of the plant undoubtedly absorb aldehyde vapor. This assimilation can take place in the absence of both oxygen and light.

Likewise Grafe and Vieser[47] have grown seedlings of *Phaseolus vulgaris* in air free from carbon dioxide but containing formaldehyde and report that plants under such conditions grow more rapidly than in normal air.

So far as I know, no attempts have been made to ascertain the effect of glycolaldehyde and glycerose upon the growth of the plant. It is probable that these compounds are intermediate products in the formation of a sugar by the polymerization of formaldehyde. One would naturally expect therefore that they would be assimilated by the growing plant. Moreover, they would be better adapted than formaldehyde for such investigations, since they are relatively less toxic, and hence could be used in larger amounts.

## SYNTHETIC PRODUCTION OF SUGAR FROM FORMALDEHYDE

It will be recalled that Butlerow's methylenitan was synthesized not from formaldehyde itself but from a closely related compound, trioxymethylene. Loew[48] in 1886 was the first to build up a sugar directly from formaldehyde, using mild alkalis as condensing agents. Three years later Loew[49] succeeded in obtaining a purer product (formose) by using the oxides of lead and magnesium as condensing agents. In the meanwhile Fischer[50] was carrying out those brilliant researches in which the

[42] *Compt. rend.*, 136, p. 1155.

[43] "Flora," 92, p. 73.

[44] *Proc. Royal Soc.*, B, 77, p. 370.

[45] *Arch. ges. Physiol. (Pflügers)*, 125, p. 467.

[46] *Arch. ges. Physiol. (Pflügers)*, 128, p. 565.

[47] *Ber. d. bot. Gesell.*, 27, p. 431.

[48] *J. prakt. Chem.*, 33, p. 321.

[49] *Ber. d. chem. Gesell.*, 22, p. 475.

[50] *Ber. d. chem. Gesell.*, 20, pp. 1093, 2566, 3384.

synthesis of fructose was effected first from acrolein and later from glycerol. The whole subject of the action of alkalis upon formaldehyde has been taken up in recent years by Euler,[51] who has made a careful study of the course of the reaction and the conditions affecting it. It is especially interesting to note that this investigator has succeeded in synthesizing a sugar from formaldehyde through the agency of calcium carbonate as a condensing agent. The interest here lies chiefly in the fact that the formation of sugar may be effected by a substance universally distributed in the soil. It is interesting to note that Euler in this way showed that the simplest of sugars, viz., glycolaldehyde, is produced as an intermediate product. The principal sugar finally formed is a pentose, namely, (*dl*)-arabino-ketose. Löb[52] has recently effected similar condensations by the use of zinc as well as zinc carbonate.

Equally important are the results which have been obtained through the action of the silent electric discharge. Berthelot,[53] in this way, produced from a mixture of carbon dioxide, water and hydrogen a substance having the properties of a carbohydrate. With carbon monoxide and hydrogen he obtained a similar product which appeared to be a polymer of formaldehyde. Likewise Slosse,[54] from carbon monoxide and hydrogen, obtained a crystalline, fermentable sugar.

The investigations of Löb[55] in which he produced formaldehyde directly from carbon dioxide and water vapor through the influence of the silent electric discharge have already been referred to. Under the same conditions this investigator has been able to polymerize the aldehyde so formed into glycolaldehyde and this in turn into a hexose. The formation of a sugar from carbon dioxide and moisture has thus been effected through the agency of the energy of the silent electric discharge. It may be added that patents have been taken out for the synthetic production of sugar under this general method.

Taken as a whole, the results of the investigations would seem to corroborate Baeyer's original assumptions. The transformation of carbon dioxide and water into formaldehyde and the subsequent polymerization of this into a sugar under conditions approximating those existing in the plant may be regarded as accomplished. While the evidence advanced can not be regarded as showing beyond doubt the presence of free formaldehyde in the plant, yet it is plain that the failure to detect its presence can not be regarded as fatal or as even opposed to Baeyer's theory. In fact, one would naturally expect that because of its great activity, its polymerization would keep pace with its formation and that the tests for its presence would therefore be negative. On the other hand, it can not be doubted but that plants have the power to directly assimilate formaldehyde. While certain objections have been urged against Baeyer's hypothesis and other radically different ones[56] have been advanced, yet it would seem from the present indications that further progress in our knowledge of the formation of carbohydrates in the vegetable kingdom probably will be made along the lines originally pointed out by Baeyer.

In the study of the results of these investigations one is impressed with the large number of conflicting statements. Certainly one would not turn to these re-

[51] *Ber. d. chem. Gesell.*, 39, pp. 39, 45.

[52] *Biochem. Zeit.*, 12, p. 78.

[53] *Compt. rend.*, 126, p. 610.

[54] *Bull. de l. Ac. roy. de Belg.*, 35, p. 547.

[55] *Zeit. f. Elektrochem.*, 12, p. 282.

[56] Etard, "La Biochem. et les chlorophylles," Paris, 1906; Loew, "Chem. Energ. in leb. Zell.," 1906.

ports as an argument for the exactness of chemical science. As a rule, however, the disagreements relate not so much to the observations as to their interpretation. Of course it is useless to expect investigators to agree upon the question as to whether or not formaldehyde is present in the plant, until they first can agree in regard to the tests for formaldehyde which shall be considered as conclusive. Again while this general subject is primarily a chemical one, yet many of the investigators have been men trained rather in other fields of work. It would seem that the chemist, or better, perhaps, the chemist and the botanist working conjointly, ought to be able to make surer progress in such investigations. The problem is an exceedingly complex one. Its solution involves many reactions at present but little understood—such as the nature of catalytic and enzymic action and the formation of asymmetric compounds. It is probable also that other forces not yet investigated may enter into the reactions by which these compounds are formed. Stewart[57] has even suggested that it is "not improbable that the rotation of the earth or terrestrial magnetism or the motion of the earth around the sun may have some effect." There is no doubt, however, but that progress is being made. It is also undoubtedly true that many of the researches now being carried on in our laboratories will be found to have a more or less direct bearing upon the general question; and it has been partly my object in discussing this topic to emphasize this fact in order that the results of our investigations, whenever applicable, may be directed towards the solution of this problem.

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[57] "Stereochemistry," London, 1907, p. 535.

## THE AMERICAN MUSEUM OF NATURAL HISTORY

Dr. Hermon C. Bumpus has resigned the directorship of the American Museum of Natural History and has accepted the position of business manager to the University of Wisconsin. This announcement was made on January 20 by Mr. Seth Low, chairman of a special committee of the trustees appointed to consider the administration of the museum. He gave out the following statement:

Director Bumpus notified the trustees of the American Museum of Natural History at a special meeting held yesterday afternoon that he had accepted an appointment as business manager for the University of Wisconsin. Accordingly he presented his resignation as director, which was accepted. The administrative difficulty in the museum is thus terminated.

The questions raised as to the respective duty and authority of various officers in the museum seemed to the board important enough to be referred to a special committee, which was appointed on November 30, 1910, to give a hearing to the director and to consider his criticisms. The committee, which consisted of Anson W. Hard, Adrian Iselin, Jr., Percy R. Pyne, Felix M. Warburg and Seth Low (chairman), went into every criticism very thoroughly. They found nothing to justify the sweeping statements which had been made, and the specific criticisms of President Osborn, when sifted, were found to be either unimportant or not sustained. The committee and the board believes that the administration of President Osborn has been wise, efficient, far-sighted and public-spirited, and that the financial management has been sound and constructive.

## THE CARNEGIE INSTITUTION OF WASHINGTON

It was announced on January 20 that Mr. Andrew Carnegie had added $10,000,000 to the endowment fund of the Carnegie Institution of Washington. The institution was established in 1902 with a gift of $10,000,000, and Mr. Carnegie recently added $2,000,000. These gifts consist of preferred bonds of the Steel Corporation bearing five per cent. interest and their market value is considerably above their par value. Mr. Carnegie's gifts to